Vibrational spectroscopy and solubility study of the mineral stringhamite $CaCuSiO_4 \cdot H_2O$

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ABSTRACT

Stringhamite $CaCuSiO_4 \cdot H_2O$ is a hydrated calcium copper silicate and is commonly known as a significant 'healing' mineral and is potentially a semi-precious jewel. Stringhamite is a neosilicate with Cu^{2+} in square planar coordination. Vibrational spectroscopy has been used to characterise the molecular structure of stringhamite.

The intense sharp Raman band at 956 cm^{-1} is assigned to the ν_1 (A_{1g}) symmetric stretching vibration. Raman bands at 980, 997, 1061 cm^{-1} are assigned to the ν_3 (A_{2u}, B_{1g}) antisymmetric stretching vibrations. Splitting of the ν_3 vibrational mode supports the concept that the stringhamite SiO_4 tetrahedron is strongly distorted. The intense bands at 505 and 519 cm^{-1} and at 570 cm^{-1} are assigned to the ν_2 and ν_4 vibrational modes.

The question arises as to whether the mineral stringhamite can actually function as a healing mineral. An estimation of the solubility product at pH < 5 shows that the cupric ion can be released. The copper ion is a very powerful antibiological agent and thus the mineral stringhamite may well function as a healing mineral.

Key words: stringhamite, cupric ions, healing mineral, vibrational spectroscopy, chrysocolla

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Introduction

There are a significant number of silicate minerals which have copper as one of the principal cations. These include chrysocolla $(Cu, Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O$, dioptase $CuSiO_3 \cdot H_2O$, planchéite $Cu_8Si_8O_{22}(OH)_4 \cdot H_2O$, shattuckite $Cu_5(SiO_3)_4(OH)_2$,whelanite $Ca_5Cu_2(OH)_2CO_3,Si_6O_{17} \cdot 4H_2O$, ajoite $(K,Na)Cu_7AlSi_9O_{24}(OH)_6 \cdot 3H_2O$, apachite $Cu_9Si_{10}O_{29} \cdot 11H_2O$ and stringhamite $CaCuSiO_4 \cdot H_2O$. Apart from chrysocolla which appears as an amorphous non-diffracting mineral, all of these copper silicate minerals are highly crystalline and contain either hydroxy units or water units or both. These water and OH units are important for the stability of the minerals. All these minerals are of various shades of blue. A common feature of these minerals is that these copper containing silicate minerals are used as 'healing' minerals [1]. Copper is very important in human health but is toxic at higher concentrations [2]. Copper ions are of course a very powerful antibacterial agent [1, 3, 4]. Copper compounds are used as antibacterial agents. Estimation of the amount of copper in water and foods has been measured [5, 6]. A major issue with these minerals is that studies of their molecular structure are unknown or very limited. Vibrational spectroscopic studies of the minerals such as stringhamite have not been forthcoming.

Stringhamite [7] is monoclinic with point group 2/m, and space group: $P2_1/c$, a = 5.030(2), b = 16.135(3), c = 5.343(1), β= 102:96(1) and Z = 4 [8]. Well formed azure crystals are found but smaller than 0.1 mm, dominated by 011 and 101 directional growth (page 760) [9]. According to Hawthorne [8], stringhamite is a neosilicate with Cu^{2+} in square planar coordination and Ca in [7]-coordination that approximates a diminished square antiprism. The fundamental building block of the stringhamite structure is a $[Cu(SiO_4)O_3]^{8-}$ heteropolyhedral cluster that polymerizes in 2 dimensions by corner-sharing between the squares and tetrahedra to form the structure module, a $[Cu(SiO_4)]^{2-}$ heteropolyhedral sheet parallel to (010). These sheets are linked by hydrogen bonding and by calcium ions.
To date there have been few spectroscopic studies of stringhamite. Vedanand *et al.* undertook optical and EPR spectra of stringhamite [10]. These researchers collected the infrared spectra of stringhamite and proposed the spectra depended upon the SiO_4 tetrahedra which is strongly affected by the distortion of copper(II) ion in octahedral to square planar field. Vedanand *et al.* [10] observed bands in the optical spectrum at 22 200, 15 620 and 14 280 cm^{-1} due to Cu(II) ion and assigned the transitions, $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{2g} \rightarrow {}^2B_{2g}$

respectively. The crystal field parameters *Dq* and tetragonal field parameters *Ds* and *Dt* are evaluated as 1428, 3362 and 1749 cm^{-1} respectively. EPR spectrum of stringhamite revealed a single peak with $g = 2.003$. The unresolved EPR spectrum is due to the high concentration of copper [*CuO* = 31.6%] in stringhamite. Hindman reported the infrared spectrum of stringhamite [7] and identified two peaks at 2890 and 3150 cm^{-1} and assigned the bands to water. Hindman observed a strong infrared band at 800 cm^{-1} but no definitive assignment was made. Vibrational spectroscopic studies of the mineral stringhamite are lacking.

Vibrational spectroscopy has proven very useful for the study of the molecular structure of minerals [11-17]. Indeed Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with minerals containing copper and silicate groups. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. The objective of this research is to report the Raman spectra of stringhamite and to relate the spectra to the molecular structure of the mineral.

Experimental

Mineral

The mineral stringhamite was supplied by the Mineralogical Research Company. The mineral originated from the Christmas Mine, Gila County, Arizona, USA. The mineral sample is defined as a 'type' mineral and is used as a reference for this type of mineral and its structure. Details of the mineral have been published (page 142) [9].

Raman spectroscopy

Crystals of stringhamite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The crystals of stringhamite are quite small and so the spectra are collected from a group of crystals. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 200 and 4000 cm^{-1}. The power used at the sample was 0.1 mW. Repeated

acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio of the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio. The infrared spectra are given in the supplementary information.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian-Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and Discussion

The Raman spectrum of stringhamite in the 100 to 4000 cm^{-1} region is displayed in Figure 1a. The spectrum shows the relative intensity of the Raman bands. The intensity in the OH stretching region is low. It may be observed that much of the spectrum is blank, and consequently the spectra are divided into sections for a more detailed analysis. The infrared spectrum of stringhamite is reported in Figure 1b. Again the relative intensities of the infrared bands may be observed and a comparison of intensities with the Raman spectrum observed. Again in the infrared spectrum, there are whole sections where no bands are observed. The spectra are subdivided into sections for more detail.

The Raman spectrum of stringhamite in the 800 to 1400 cm^{-1} region is shown in Figure 2a. The spectrum consists of a series of sharp bands, most of which are the vibrational modes of SiO_4 units. In contrast the infrared spectrum of stringhamite in the 500 to 1300 cm^{-1} region is displayed in Figure 2b. The infrared spectrum consists of a series of overlapping bands. The intense sharp band at 956 cm^{-1} is assigned to the ν_1 (A_{1g}) symmetric stretching vibration. Vedanand et al. observed a band at 800 cm^{-1} and defined this band to be the ν_1 vibration. However this does not appear to be in agreement with this work. The band appears as a low intensity shoulder in the infrared spectrum at 961 cm^{-1}. According to Farmer [18], this band for zircon is observed at 974 cm^{-1}. As pointed out by Vedanand *et al.* [10], the distorted Cu^{2+} ion effects the symmetry of the SiO_4 units. This results in a shift in band position to lower wavenumbers. The EPR results of Vedanand *et al.* prove that the Cu^{2+} ion is in a square planar environment and the bonding between the Cu^{2+} ion and the oxygen ligands in the square planar coordination is very strong. Raman bands at 980, 997, 1061 cm^{-1} are assigned to the ν_3 (A_{2u}, B_{1g}) antisymmetric stretching vibrations. The Raman band at 908 cm^{-1} is assigned to the ν_3 (E_u) vibration. The equivalent infrared bands are identified at 997, 1055 and 1082 cm^{-1}. The assignment of these bands is in good agreement with that of Vedanand *et al.* these workers observed a sharp infrared band at 1020 cm^{-1} with shoulders at 1040 and 1090 cm^{-1}. The infrared spectrum consists of a series of overlapping band with bands curve resolved at 749, 829, 876, 918 cm^{-1}. The splitting of the ν_3 vibrational mode offers support to the concept that the SiO_4 tetrahedron in stringhamite is strongly distorted. This concept is further supported by the observation of multiple ν_4 bands at around 600 cm^{-1}. For a perfectly symmetric SiO_4 tetrahedron, only a single band at 608 cm^{-1} (A_{2u}) should be observed. Infrared bands are found at 577, 590, 597, 629 and 639 cm^{-1}. Other bending modes occur below 500 cm^{-1} which is below the lower limit of the ATR technique. Vedanand *et al.* reported the ν_2 and ν_4 modes at 510 and 660 cm^{-1}.

These ν_4 bands are more easily observed in the Raman spectrum (Figure 3). An intense band at 570 cm^{-1} is assigned to the ν_4 vibrational mode. Some sharp but low intensity Raman bands at 626 and 693 cm^{-1} may also be attributed to this vibrational mode. The strong bands at 505 and 519 cm^{-1} are assigned to the ν_2 vibrational modes. According to Farmer [18], the ν_2 in-plane bend for a perfect SiO4 tetrahedron should be found at 439 cm^{-1}. Vedanand *et al.* observed an infrared band at 510 cm^{-1} and assigned the band to the ν_2 vibrational mode. The splitting of the ν_2 vibrational mode supports strongly the concept of a strongly distorted SiO_4 tetrahedron. The Raman bands at 303, 369, 396 and 431 cm^{-1} are attributed to CuO and CaO

stretching vibrations. The observation of two bands at 369 and 396 cm^{-1} shows that not all the Cu ions in the stringhamite structure are equivalent. In terms of the molecular structure the Cu^{2+} ions are in different positions.

The Raman and infrared spectra of the OH stretching region are displayed in Figure 4a and 4b respectively. The Raman spectrum lacks signal to noise; however this is not unexpected as water is a poor Raman scatterer and the intensity of the bands is predicted to be weak. Two Raman bands are observed at 3193 and 3239 cm^{-1} and are assigned to water stretching vibrations. The infrared spectrum displays much greater complexity with two principal bands observed at 2610 and 3177 cm^{-1}. There is a band at around 2650 cm^{-1} in the Raman spectrum but is lost in the noise. Vedanand *et al.* found infrared bands at 2860, 2930 and 3400 cm^{-1} and assigned the bands to water stretching vibrations. The observation of the infrared band at 2610 cm^{-1} shows that water is very strongly hydrogen bonded in the stringhamite structure.

Stringhamite as a healing mineral

Is there any truth in the statement that stringhamite is a healing mineral[1]? There is certainly a great deal of literature on the subject, especially on the internet [2, 19]. It is well known that Cu^{2+} is a very powerful antibacterial agent [4, 20, 21]. Copper compounds are used as fungicides. It is well known that copper is essential for human health, although too much copper can be toxic [2]. Copper compounds are used as antibacterial agents in swimming pools and is a powerful antibacterial agent in open latrines. Copper compounds are hazardous to aquatic organisms.

In the laboratory, silicate minerals are shown to dissolve in hydrolysis reactions.
For example: $KAlSi_3O_8 + 4H^+ + 4H_2O = K^+ + Al^{3+} + 3H_4SiO_4$
The dissolution of orthoclase, as shown above, occurs through a hydrolysis reaction driven only by pH. Because reaction rates depend on the chemical potential, the rate at which orthoclase dissolves in hydrolysis reactions is a function of pH.

The question arises as to whether a mineral such as stringhamite can provide very low concentrations of copper ions. The following reaction is envisaged:
$CaCuSiO_4 \cdot H_2O + 2\,H^+ \rightarrow Cu^{2+} + CaSiO_3 + H_2O$

The reaction above depends upon exchange of copper ions with other ions such as the hydrogen ion in an aqueous medium. In effect, the equation represents acid leaching. The above chemical reaction offers a mechanism for the release of Cu^{2+} ions.

Even if very low concentrations of Cu^{2+} ions exist, it means that the mineral can function as a healing mineral. If we use a simplified form of stringhamite, namely $CuSiO_3 \cdot H_2O$ (as is given in the introduction), then the following reaction can occur:

$$CuSiO_3 \cdot H_2O + 2H^+ = Cu^{2+} + H_4SiO_4$$

$$K_{(sp)} = [Cu^{2+}][H_4SiO_4]/[H^+]^2$$

If we take the value of the solubility product to be a small number such as 10^{-20}, then appropriate calculations can be made. At pH=4, then

$$10^{-20} = [Cu^{2+}]^2/10^{-4}$$

Thus, $[Cu^{2+}] = 10^{-8}$

What this reaction and the calculations prove is that under acid conditions copper silicate minerals can release copper ions to the environment. So if the mineral stringhamite for example is rubbed on the skin, the acidity of the skin will release copper ions. In other words, there is evidence that the mineral chrysocolla acts as a healing mineral.

CONCLUSIONS

The mineral stringhamite $CaCuSiO_4 \cdot H_2O$ is renowned as a healing mineral. The mineral is a hydrated copper silicate. Based upon the vibrational spectroscopy of the hydroxyl stretching region, water is involved in very strong hydrogen bonding in stringhamite structure.

This research based upon solubility product studies proves that under acid conditions, even slightly acid conditions, copper ions can be released from the mineral. Since copper ions are a very powerful antibiological agent, stringhamite is indeed a healing mineral.

Acknowledgments

The financial and infra-structure support of the Queensland University of Technology, Chemistry discipline is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation.

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Figure 4 (a) Raman spectrum of stringhamite in the 2600 to 3800 cm^{-1} range (b) Infrared spectrum of stringhamite in the 2300 to 3900 cm^{-1} range

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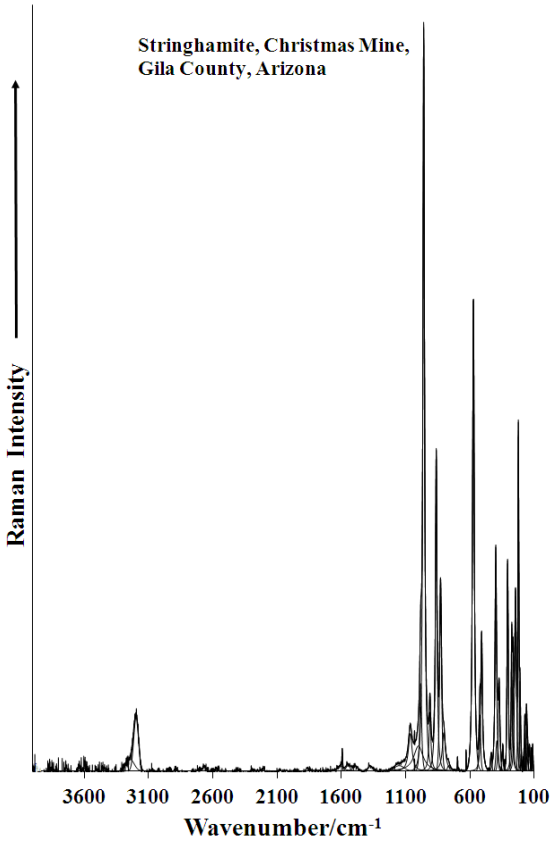

Figure 1a

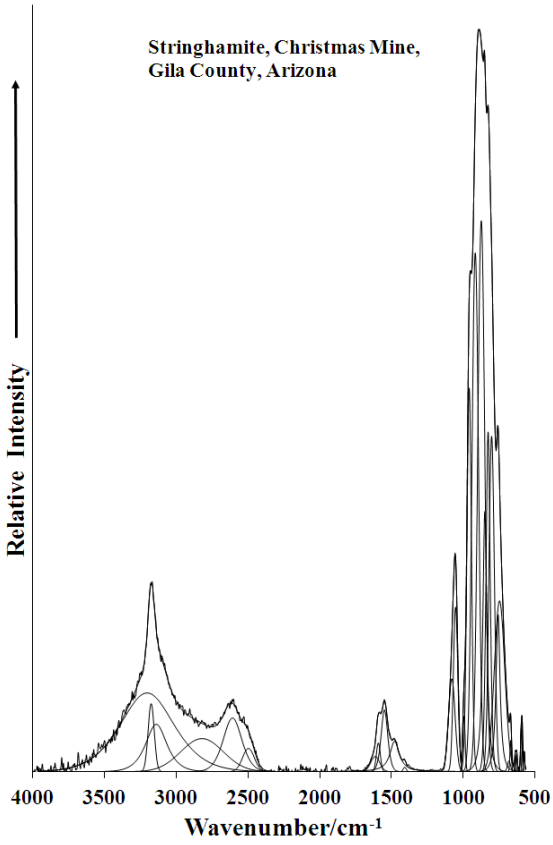

Figure 1b

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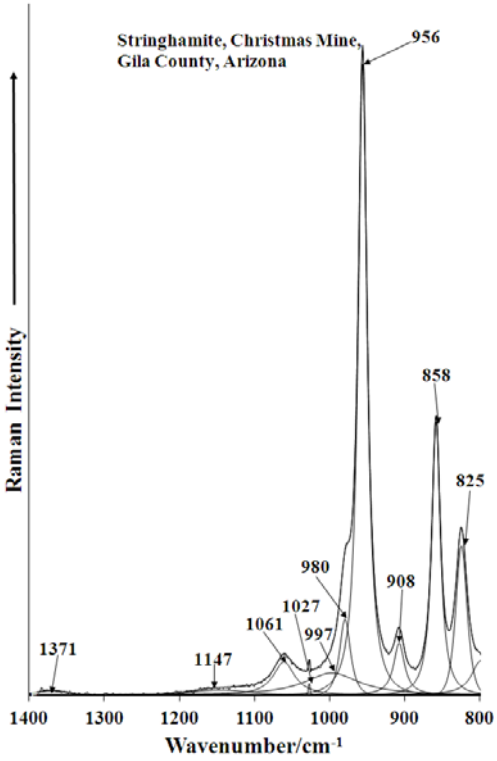

Figure 2a

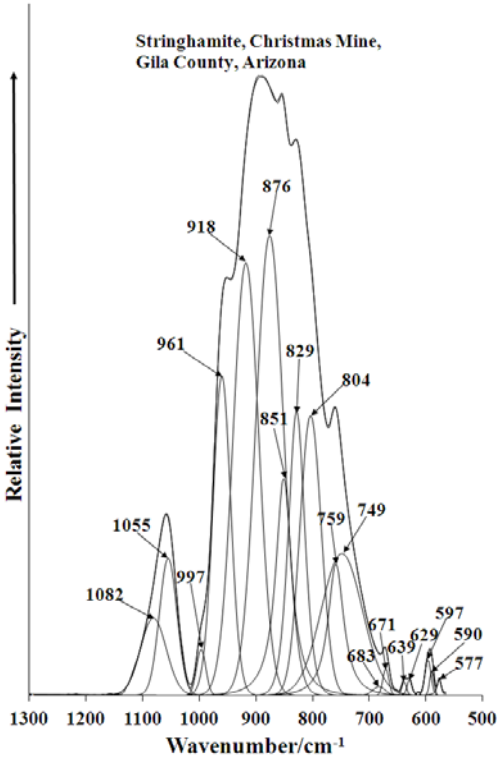

Figure 2b

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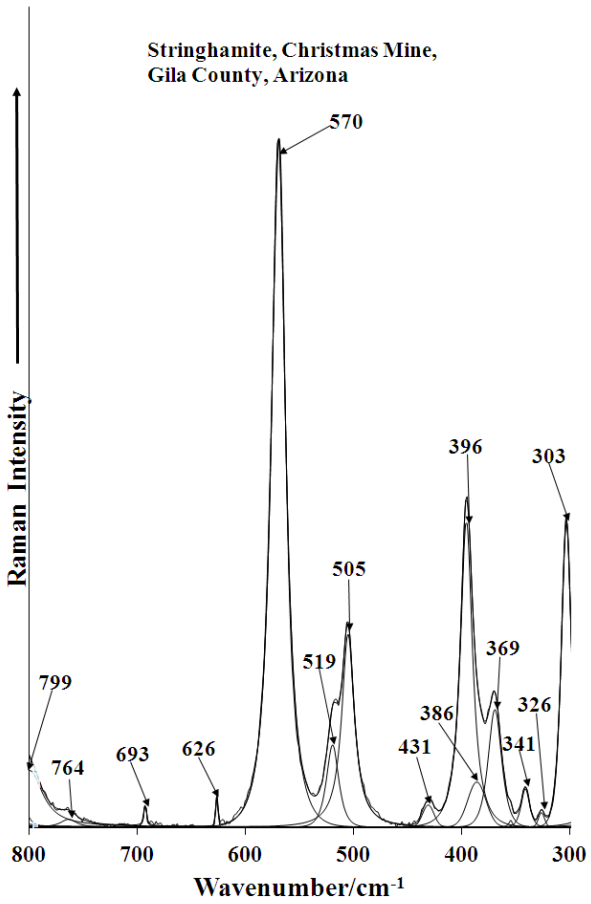
Stringhamite, Christmas Mine,
Gila County, Arizona
570
396
303
505
519
369
799
386
326
764
693
626
431
341
Raman Intensity
800
700
600
500
400
300
Wavenumber/cm-1

Figure 3

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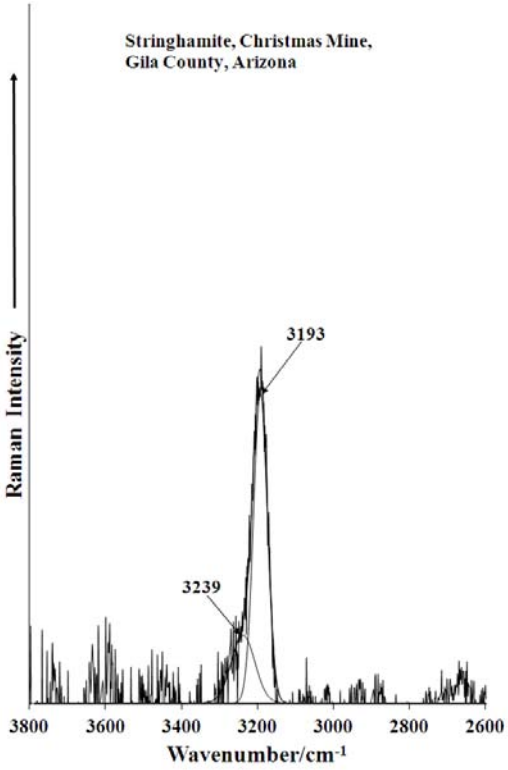

Figure 4a

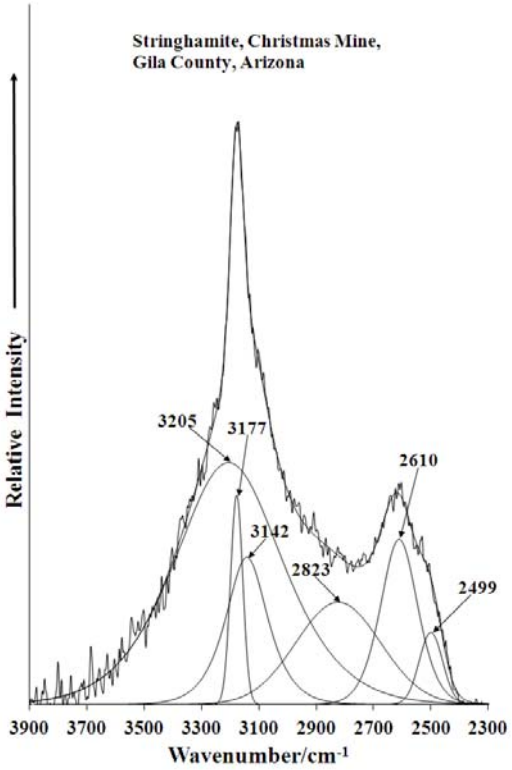

Figure 4b

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